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Microwave assisted modification of activated carbons by organic acid ammoniums activation for enhanced adsorption of acid red 18

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ABSTRACT

Three organic acid ammoniums (ammonium succinate (AS), ammonium tartrate (AT) and ammonium citrate (AC)) were employed to modify *Phragmites australis* (PA)-based activated carbons during phosphoric acid activation via microwave irradiation to improve acid red 18 (AR 18) removals from aqueous solutions. The physicochemical properties of the modified (PAC-AS, PAC-AT and PAC-AC) and unmodified carbons (PAC) were systematically characterized. The nitrogen content, pH_{iep} and basic foundational groups of the modified carbons increased however their surface areas decreased after modification. FTIR and XPS analyses revealed that N-containing groups such as —NH, —CONH— and —NH_2 were effectively introduced on modified carbons' surfaces. Although PAC-AS and PAC-AT had lower surface area than PAC, their adsorption capacity were higher due to larger amount of N-containing groups. The adsorption kinetic data were simulated well by the Elovich equation and the equilibrium data were best fit to the Freundlich model for all PACs. The adsorption of AR 18 on PACs decreased with increasing pH values. The maximum AR 18 adsorption capacity followed an order of PAC-AS (115.93 mg/g) > PAC-AT (104.23 mg/g) > PAC (90.52 mg/g) > PAC-AC (57.99 mg/g), indicating that AS and AT are promising activating agents for activated carbons to improve their AR18 adsorption performances.

1. Introduction

Dyes have been extensively used in manufacturing industries including textile, leather, food processing, rubber and printing [1]. They are highly visible and toxic even at very low concentrations, posing a tremendous risk to human and ecosystem health. It is important to remove dyes from wastewater before they are discharged into the environment [2]. Numerical physical, chemical and biological approaches (e.g., membrane filtration, advanced oxidation, coagulation/flocculation, bioremediation, photocatalytic degradation and adsorption) have been reported for the removal of dyes [3,4]. However, synthetic dyes usually have complex aromatic structures, which make them stable to light, heat and oxidizing agents and reluctant to biodegradation [5]. As an efficient, economically favorable and reliable physicochemical treatment method, adsorption has been frequently employed for the removal of dyes.

Among various adsorbents, activated carbon has shown great advantages over other adsorbents for its high specific surface area and adsorption capacity. Recently, there is an increasing interest in the application of biomass wastes as precursors to prepare effective activated carbons because of environmental protection and low cost. Various carbonaceous materials such as walnut woods [3], coconut coir [6], flax shive [1], and mushroom root [7] have been exploited for the removal of dyes from aqueous solutions. Porosity and surface chemical properties are key factors that greatly influence the activated carbons' adsorption performance [8]. Hence, various approaches including activation, surface modifications and hydrothermal synthesis have been explored to improve the activated carbons' adsorption capacity or selectivity [9]. Surface modifications of activated carbons have been recognized as effective methods and receive extensively attentions recently [10]. Phosphoric acid is one of the most commonly used activating agents for producing activated carbons due to its low activation temperature and reduced pollution [11].

The O-containing functional groups (carboxylic, carbonyl, lactonic, and phenolic groups), as well as N-containing functionalities (amide, imide, lactam, pyrrolic, and pyridinic groups), can significantly change the porosity and/or acidic–basic property of the carbon materials and enrich the contaminant adsorption affinity and capacity through electrostatic attraction, surface complexation and other interactions [2,12,13]. It was reported that strong acids, such as HNO_3, $KMnO_4$, H_2O_2 or H_3PO_4, can introduce a greater amount of O-containing functional groups on the carbons' surface and elevate contaminant adsorption capacity [14]. Numbers of researchers have successfully doped nitrogen onto the carbons' surfaces by modifying carbons with

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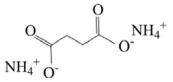
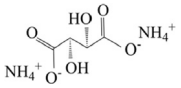
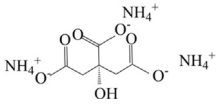
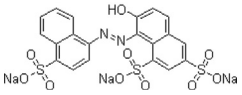
Table 1
Physical properties of activating agents and dyes.

Chemicals	Molecular formula	Abbreviation	Molecular weight (g/mol)	Structure
Phosphoric acid	H_3PO_4	PPA	97.97	
Ammonium succinate	$C_4H_{12}N_2O_4$	AS	152.15	
Ammonium tartrate	$C_4H_{12}N_2O_6$	AT	184.15	
Ammonium citrate	$C_6H_{17}O_7N_3$	AC	243.22	
Acid red 18	$C_{20}H_{11}N_2Na_3O_{10}S_3$	AR18	604.47	

NH_3, urea, or N-containing organic polymers and ionic liquids and therefore the adsorption of dyes in wastewater has been greatly improved [15,16].

Organic acid ammoniums such as ammonium succinate (AS), ammonium tartrate (AT) and ammonium citrate (AC) contain C═O and —NH groups may easily bind on the carbon's surface or generate O/N-containing groups during the activation process. To the best of our knowledge, no relevant works have been reported to use organic acid ammoniums as O/N doped resources to modify activated carbons. Besides, most of the modification methods were carried out in the conventional furnaces, which was complicated and time-consuming. The newly developed microwave-assisted pyrolysis may help overcome the shortcoming of conventional heating methods because of its short treatment time (<10 min) and reduction in energy and inert gas consumption [17–19].

The objective of this work is to obtain high performance activated carbons by using organic acid ammoniums (AS, AT and AC) mixed phosphoric acid as activating agents via microwave irradiation. The activated carbons' physical and chemical properties and their ability to remove acid red 18 were systemically examined. Acid red 18 (AR18) was chosen as the model adsorbate because of its wide application in the textile industry and well-known adsorption characteristics [20]. *Phragmites australis* (PA) was selected as precursor due to its porous caudex system and ubiquitous occurrence in wetlands of China [4].

2. Methodology

2.1. Materials

Phragmites australis (PA), a common hydrophyte, was harvested from Chan Ba wetland located in Shaanxi province, China. The biomass was cleaned with deionized water several times to remove dust and impurity. After drying at 80 °C for 24 h, the sample was pulverized into small pieces (particle sizes of 0.25–0.45 mm) in a steel blender (LG-20, Zhejiang, China). Four activating agents were chosen for PA activated carbon preparation, including phosphoric acid (PPA, 85%) and three organic acid ammoniums (ammonium succinate (AS), ammonium tartrate (AT) and ammonium citrate (AC)). Their basic physical properties are listed in Table 1. All the chemicals used in this work were of analytical grade and solutions were prepared with deionized water.

2.2. Preparation of activated carbons

PA (15 g) was immersed in H_3PO_4 solution (85 wt%) at the ratio of 2:1 (g H_3PO_4:g PA) and with 0.04 mol AS/AT/AC for 10 h at room temperature. The impregnation ratio and time were chosen based on the Guo et al.'s work where the maximum functional groups were obtained [4]. Then the samples were put in a silicon carbide dry pot and heated in a microwave oven (MKX-M1B, Qingdao, China) at 700 W for 15 min

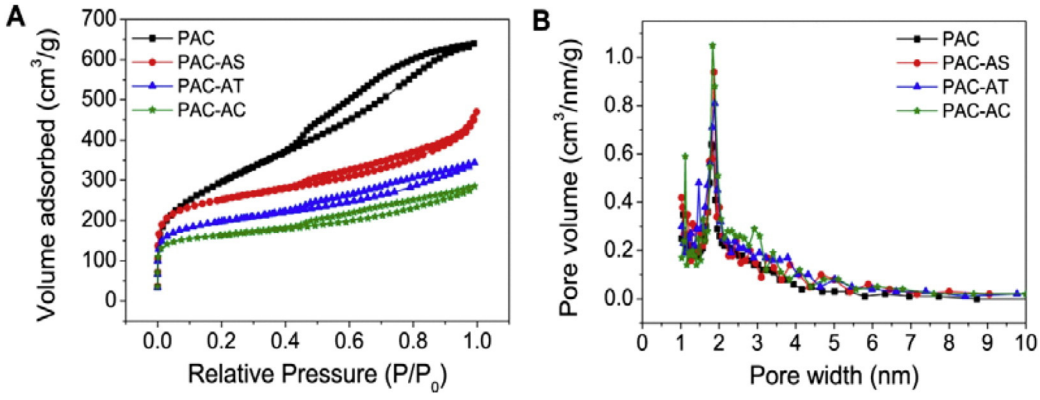


Fig. 1. N_2 adsorption and desorption isotherms (A) and pore size distributions of the activated carbons (B).